JC14 Rec'd PCT/PTO 20 DEC 2001

FORM PTO-1390 OFFICE (REV 11-2000) U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK	ATTORNEY'S DOCKET NUMBER 300602002300
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. § 371	U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 10/018426 to be assigned

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/KR00/00983	**30 August 2000**	**21 April 2000**

TITLE OF INVENTION
LOW TEMPERATURE SINTERABLE AND LOW LOSS DIELECTRIC CERAMIC COMPOSITIONS AND METHOD THEREOF

APPLICANT(S) FOR DO/EOUnited States
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Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [x] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. [ ] This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. [ ] The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).
5. [x] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. [x] is attached hereto (required only if not communicated by the International Bureau).
   b. [ ] has been communicated by the International Bureau.
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [ ] An English language translation of the International Application under PCT Article 19 (35 U.S.C. 371(c)(2)).
   a. [ ] is attached hereto.
   b. [ ] has been previously submitted under 35 U.S.C. 154(d)(4).
7. [ ] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
   a. [ ] are attached hereto (required only if not communicated by the International Bureau).
   b. [ ] have been communicated by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [ ] have not been made and will not be made.
8. [ ] An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. [ ] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [ ] An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. [x] An Information Disclosure Statement under 37 CFR 1.97 and 1.98 and Form PTO 1449 (copies of references to be provided)
12. [ ] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [ ] A FIRST preliminary amendment.
14. [ ] A SECOND or SUBSEQUENT preliminary amendment.
15. [ ] A substitute specification.
16. [ ] A change of power of attorney and/or address letter.
17. [ ] A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. [ ] A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. [ ] A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. [x] Other items or information: PCT/IB/301, PCT/IB/304, PCT/IB/308, International Search Report, and Application Data Sheet

CERTIFICATE OF HAND DELIVERY

I hereby certify that this correspondence is being hand filed with the United States Patent and Trademark Office in Washington, D.C. on December 20, 2001.

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JC13 Rec'd PCT/PTO 20 DEC 2001

U.S. APPLICATION NO. (if known, see 37 CFR 1.5) to be assigned 10/018426	INTERNATIONAL APPLICATION NO. PCT/KR00/00983	ATTORNEY DOCKET NUMBER: 300602002300

	CALCULATIONS	PTO USE ONLY
21. ☒ The following fees are submitted: **BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):** Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ....$1,040.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ....$890.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ....$740.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provision of PCT Article 33(1)-(4) ....$710.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) $100.00		
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CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	9 - 20 =	--	x $18.00	$--	
Independent claims	4 - 3 =	1	x $84.00	$84.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ $280.00	$	
TOTAL OF ABOVE CALCULATIONS =				$974.00	
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SUBTOTAL =				$487.00	
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December 20, 2001

10/018426
JC13 Rec'd PCT/PTO 20 DEC 2001

WO 01/81269

7/prts

PCT/KR00/00983

LOW TEMPERATURE SINTERABLE AND LOW LOSS DIELECTRIC CERAMIC COMPOSITIONS AND METHOD THREOF

TECHNICAL FIELD

The present invention relates a high frequency dielectric ceramic compositions.

BACKGROUND ART

Recently, with the rapid development in a mobile communication and a satellite communication, a high frequency dielectric ceramics is in a high demand as a material for a high frequency integrated circuit or a dielectric resonator.

Major characteristics of the dielectric ceramics used for a high frequency includes a high dielectric constant (ε_r), a quality factor (Q) and a stable and tunable temperature factor (τ_f) of a resonance frequency.

Representative high frequency dielectric compositions which have been widely known up to now are (Zr, Sn)TiO_4 group, BaO-TiO_2 group, (Mg, Ca)TiO_3 group, and Ba-$(Zn_{1/3}Ta_{2/3})O_3$, $Ba(Mg_{1/3}Ta_{2/3})O_3$, $Ba(Zn_{1/3}Nb_{2/3})O_3$ as Ba-peropskite group.

However, these compositions are disadvantages in that they are mostly fired at a high temperature of 1,300~1,500°C, upper sum is not easy, a dielectric constant is low or a high-priced material should be used.

Besides, lately, advancement of a portable information communication devices lead to development of various types of boards and multi-chip module

(MCM) by a multilayer chip high frequency devices or low temperature co-firing ceramics (LTCC), and a research and development of a low temperature firing high performance high frequency ceramics are conducted accordingly.

However, there are problems that the performance of the high frequency characteristic is considerably degraded such as, for example, most of them are not sufficient in terms of density when being fired at a low temperature, a dielectric constant is degraded according to addition of a firing material, a quality factor is degraded and a temperature factor is changed.

In addition, silver conduct or copper conduct with a small high frequency loss and a cofiring available low temperature firing high frequency dielectric ceramic are very rare.

Therefore, an object of the present invention is to provide a dielectric ceramics composition which can be fired at a very low temperature but has an excellent high frequency dielectric characteristic of various temperature compensation characteristics according to a high quality factor, a dielectric constant, a stable temperature factor and a composition, and can be implemented at a low cost.

Another object of the present invention is to provide a dielectric ceramics composition which can employ Ag, Cu, their alloy or a Ag/Pd alloy as an internal electrode and thus be used for various high frequency devices, such as a stacked chip capacitor, a stacked chip filter, a stacked chip capacitor/inductor composite device and a low temperature firing board, a resonator and a filter or a ceramic antenna.

DETAILED DESCRIPTION OF THE INVENTION

In order to achieve the above objects, there is provided a dielectric ceramics composition which is constructed by combining 1 mole of $(Zn_{1-x}M_x)TiO_3$ and $yTiO_2(0 \leq y \leq 0.8$ and fired at a low temperature of 925~1,100°C, its preparation method, and a high frequency dielectric ceramics device using the same. In this respect, 'M' is one of Mg, Co, Ni, 'x' is $0 \leq x \leq 0.6$ in case of Mg and 'x' is $0 \leq x \leq 1$ in case of Co, and $0 \leq x \leq 1$ in case of Ni

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing a method for determining a phase dissociation temperature from a DSC curve.

Figure 2 is a graph showing a phase dissociation temperature of $(Zn_{1-x}Mg_x)TiO_3$ according to a substituted amount of Mg;

Figure 3 is a graph showing a DSC curve of $(Zn_{0.8}Mg_{0.2})TiO_3$ composition;

Figure 4 illustrates an XRD pattern obtained when $(Zn_{0.8}Mg_{0.2})TiO_3$ is heat-treated at a temperature of 1000°C for 4 hours;

Figures 5A and 5B illustrate XRD patterns each obtained after $(Zn_{1-x}Co_x)TiO_3$ is calcined at temperatures of 1000°C and 1150°C for four hours;

Figures 6A and 6B illustrate XRD patterns each obtained after $(Zn_{1-x}Ni_x)TiO_3$ is calcined at temperatures of 1000°C and 1150°C for four hours;

Figure 7 is a graph showing a microwave dielectric characteristic of $(Zn_{1-x}Co_x)TiO_3$; and

Figure 8 is a graph showing a microwave dielectric characteristic of $(Zn_{1-x}Ni_x)TiO_3$.

MODE FOR CARRYING OUT THE PREFERRED EMBODIMENTS

The present invention will now be described with reference to accompanying drawings.

A high frequency dielectric ceramics composition of the present invention is characterized in that it has a very low firing temperature (925~1100°C) compared to that of a conventional dielectric composition, has an excellent high frequency dielectric characteristic of various temperature compensation characteristics according to a high quality factor, a dielectric constant, a stable temperature factor and a composition, and can be implemented with a low-priced material such as ZnO, MgO, CoO, NiO, TiO_2,

In addition, the high frequency dielectric ceramics composition of the present invention is also characterized in that it employs Ag, Cu, their alloy or a Ag/Pd alloy as an internal electrode and thus be used for various high frequency devices, such as a stacked chip capacitor, a stacked chip filter, a stacked chip capacitor/inductor composite device and a low temperature firing board, a resonator and a filter or a ceramic antenna.

In the present invention, the low temperature firing composition of the present invention has an excellent quality factor (close to the existing high temperature firing composition) more than several times the existing one. In addition, in the claimed composition coverage, combination of composition

having an excellent high frequency characteristic of the almost infinite number can be obtained compared to any of the conventional ones.

$ZnTiO_3$ (crystal structure has a rhombohedral symmetry) is phase-dissolved to Zn_2TiO_4 (cubic symmetry) and TiO_2 (rutile) at a higher temperature than 945°C (refer to Fig.303 of phase diagrams for ceramist, System ZnO-TiO_2 by Dulin and Rase), and thus, it is very difficult to be prepared.

In order to obtain a pure $ZnTiO_3$, phase synthesis and firing must be made at a below 945°C. A preliminary experiment of the present invention shows a result through an X-ray diffraction analysis that phase dissociation starts at near 925°C so that a thermal treatment must be performed at below 925°C.

In the present invention, in order to remove the shortcomings, Zn^{2+}, a positive ion of A-site constituting an ABO_3 type ilmenite phase ceramics, is substituted with Mg^{2+} (up to 0.6 mole), to thereby enlarge a thermal stabilization temperature of $ZnTiO_3$ to a high temperature range (refer to Figure 2), so that the preparation process coverage is widened and the high frequency dielectric characteristic are highly improved.

A high frequency dielectric ceramics composition in accordance with a preferred embodiment of the present invention will now be described.

Material powder (an average particle diameter is 1μm) of ZnO, MO (in this respect, MO is MgO, CoO or NiO) and TiO_2 (>99%) was weighed according to a composition range of $(Zn_{1-x}M_x)TiO_3$ and $yTiO_2$ (M is one of Mg, Co and Ni, x is $0 \le x \le 0.6$ in case of Mg, x is $0 \le x \le 1$ in case of Co, x is $0 \le x \le 1$ in case of Ni, and y is $0 \le y \le 0.8$), mixed in a wet ball mill method, dried at 120°C, and calcined and

synthesized at a temperature of 850~950°C for four hours.

The calcined powder was crushed and dried for 24 hours, to which an aqueous solution with 2 wt % of PVA binder added therein was sprayed to create a granule of about 200 μm size, with which a disk test sample was shaped having a diameter of 10 mm and a thickness of 4.8MM under a pressure of 98 Mpa.

The shaped test sample was maintained at a temperature of 300~500°C for more than 3 hours to burn out the binder and fired at a temperature of 925~1100°C at an atmospheric pressure for 4 hours. At this time, a heat rising rate was 10°C/min.

The sintered test sample was ground with an SiC polishing paper (#1,500) to obtain about 0.45 ratio of diameter to thickness of the test sample.

The high frequency dielectric characteristic was measured in a $TE_{01\delta}$ mode by using a network analyzer (HP 8720C), and a dielectric constant was measure by a Hakki-Coleman method, a quality factor was measure by an open cavity method, a temperature factor of a resonance frequency was measured by an invar cavity at a temperature range of +20~+70°C.

As a method for detecting the phase dissociation temperature of a compound, a DSC (differential scanning calorimetry) was used. A measurement condition was that α-alumina was taken as a standard test sample and a test sample of about 20mg was put in a platinum (Pt) crucible and measured in an air at a heat rising rate 10°C/min.

Figure 1 is a graph showing a method for determining a phase

dissociation temperature based on a recommendation method of an ICTA from the DSC curve.

Figure 2 is a graph showing the phase dissociation temperature (T_{DC}) of $(Zn_{1-x}Mg_x)TiO_3$ according to a substituted amount of Mg, in which it is noted that a dissociation temperature is moved up to a high temperature as the amount of Mg is increased, widening a phase stability region, so that it is easy to fabricate a synthetic powder.

In case of the region 'x' = 0, $ZnTiO_3$ is dissociated at a temperature 945°C, and since the dissociation temperature is moved to a high temperature according to the substitution of Mg, a single phase of the $(Zn_{1-x}Mg_x)TiO_3$ solid solution can be easily synthesized or sintered even at the temperature of 945°C.

Accordingly, the single phase can be obtained anywhere in the range of 'region II' of Figure 2, and this region is the phase synthesis region of the present invention.

Figure 3 is a graph showing a DSC curve of $(Zn_{0.8}Mg_{0.2})TiO_3$ composition, and Figure 4 is a graph showing an XRD pattern in case that the $(Zn_{0.8}Mg_{0.2})TiO_3$ composition was heat-treated at a temperature of 1000°C for four hours, which is a single phase $(Zn_{0.8}Mg_{0.2})TiO_3$.

On the basis of the obtained result, the region 'II" of Figure 2 was selected as the phase synthesis temperature of $(Zn_{1-x}Mg_x)TiO_3$, and $0<x\leq0.1$ composition was heat-treated to be synthesized at a temperature of 900°C for four hours, $0.1\leq x\leq0.6$ composition was heat-treated to be synthesized at a temperature o 950°C for four hours. Thereafter, it was observed that

rhombohedral and/or hexagonal single phase of $(Zn_{1-x}Mg_x)TiO_3$ was formed through an XRD analysis.

Table 1 shows a microwave dielectric characteristic of $(Zn_{1-x}Mg_x)TiO_3$ $0 \leq x \leq 0.6$ composition.

In the composition range, a dielectric constant was 20~25, a quality factor was 36800~85900 GHz, and a temperature factor of a resonance frequency was -25 ~ -73 ppm/°C.

In case of a composition of x>0.6, due to an influence of the high temperature material MgO, the sintering temperature was higher than 1100°C and a dielectric constant was below 20, so that a practicality and an economical efficiency are degraded.

Table 1: A high frequency dielectric characteristic of a dielectric resonator fabricated with $(Zn_{1-x}M_x)TiO_3$ ($M = Mg$, $0 \leq x \leq 0.6$)

No.	X (mole)	Firing temperature (°C)	Dielectric constant (ε_r)	Quality factor (Zxf GHz)	Temperature factor
1	0.01	925	21	36800	-60
2	0.10	1000	25	58500	-25
3	0.15	1050	25	83600	-48
4	0.20	1050	22	82300	-67
5	0.25	1050	22	71300	-67
6	0.30	1050	21	77100	-61

7	0.35	1050	21	84100	-63
8	0.40	1050	21	88900	-73
9	0.45	1050	21	73600	-68
10	0.50	1050	20	81200	-54
11	0.55	1050	20	78200	-56
12	0.60	1100	20	85900	-55

Meanwhile, with a method for preventing reduction of the temperature compensation characteristic allowing a negative temperature factor of $(Zn_{1-x}Mg_x)TiO_3$ to be controllable to a value of a range of ±10 ppm/°C suitable for application of a high frequency device and the high quality factor and the dielectric constant, the excellent dielectric characteristics of $(Zn_{1-x}Mg_x)TiO_3$, $(Zn_{1-x}Mg_x)TiO_3+yTiO2$ ($0 \le y \le 0.8$) composite ceramics of which a temperature factor is positive (+430 ppm/°C), a dielectric constant is about 105, a quality factor is about 1000 (4 GHz) and TiO2 was added was fabricated.

Table 2 shows a high frequency dielectric characteristic of the composite ceramics, and especially, when a composition of which 'x' was in the range of 0.15~0.55, an excellent dielectric characteristic having a dielectric constant of 25~30, a quality factor of 80000~100000 GHz and a temperature factor of ±10 ppm/°C was obtained.

Table 2: A high frequency dielectric characteristic of a dielectric resonator fabricated with $(Zn_{1-x}M_x)TiO_3+yTiO_2$($M = Mg$, $0 \le x \le 0.6$)

No.	X (mole)	Y (mole)	Firing temperature (°C-4hrs)	Dielectric constant	Quality factor (Qxf GHz)	Temperature factor (τ f:ppm/°C)
13	0.01	0.2	925	23	42700	-24
14		0.3		28	29000	+9
15		0.4		29	27900	+29
16		0.6		33	24100	+53
17		0.8		35	22000	+74
18	0.10	0.2	1000	31	51900	+23
19		0.3		33	47300	+51
20		0.4		35	43700	+62
21		0.6		40	41900	+103
22		0.8		46	41300	+134
23	0.15	0.2	1050	30	80100	+4
24		0.3		32	74800	+12
25		0.4		34	68400	+42
26		0.6		39	57600	+99
27		0.8		44	55200	+128

No.	X (mole)	Y (mole)	Firing temperature	Dielectric constant	Quality factor (Qxf	Temperature factor

			(°C-4hrs)		GHz)	(τ f:ppm/°C)
28	0.20	0.2	1050	28	97700	-24
29		0.3		30	107000	+1
30		0.4		32	83900	+26
31		0.5		37	78800	+84
32		0.6		45	72100	+117
33	0.25	0.2	1050	27	83500	-22
34		0.3		28	101000	+3
35		0.4		32	84900	+28
36		0.6		37	77900	+64
37		0.8		42	70700	+104
38	0.30	0.2	1100	27	89100	-18
39		0.3		30	101600	+3
40		0.4		32	83600	+22
41		0.6		36	82000	+73
42		0.8		40	74100	+103

No.	X (mole)	Y (mole)	Firing temperature (°C-4hrs)	Dielectric constant	Quality factor (Qxf GHz)	Temperature factor (τ f:ppm/°C)
43	0.35	0.2	1100	28	84300	-17

44		0.3		30	99700	+6
45		0.4		32	90700	+19
46		0.6		36	81300	+78
47		0.8		40	73400	+112
48	0.40	0.2	1050	25	83100	-18
49		0.3		28	102500	-1
50		0.4		30	85500	+25
51		0.6		35	86500	+65
52		0.8		38	68400	+108
53	0.45	0.2	1050	25	69300	-18
54		0.3		27	80200	+6
55		0.4		29	74200	+34
56		0.6		34	72900	+60
57		0.8		37	69800	+115

No.	X (mole)	Y (mole)	Firing temperature (°C-4hrs)	Dielectric constant	Quality factor (Qxf GHz)	Temperature factor (τ f:ppm/°C)
58	0.50	0.2	1050	23	69800	-27
59		0.3		23	69200	-17
60		0.4		22	68800	-14

61		0.6		27	97400	+1
62		0.8		34	78200	+62
63	0.55	0.2	1050	21	73400	-52
64		0.3		22	82300	-39
65		0.4		22	72900	-35
66		0.6		23	72200	-18
67		0.8		25	87000	-3
68	0.60	0.2	1050	21	77100	-64
69		0.3		20	65600	-64
70		0.4		20	58500	-62
71		0.6		20	45000	-55
72		0.8		19	43200	-47

Such high frequency performance is second to $Ba(Zn_{1/3}Ta_{2/3})O_3$ or $Ba(Mg_{1/3}Ta_{2/3})O_3$ group ceramics.

Comparatively, the conventional dielectrics are sintered at a high temperature of 1500°C and use high-priced material such as Ta2O5, but the composition of the present invention uses a low-priced material. And, the most of conventional ceramics compositions obtain a usable dielectric characteristic only in limited range, while the composition of the present invention has an excellent dielectric characteristic in a wide range of solid solution without a firing material at a temperature of 1000~1100°C, and theoretically, in the present invention, combinations of an infinite number of usable high frequency dielectric

ceramics composition can be obtained. The aforementioned is about M=Mg in $(Zn_{1-x}M_x)TiO_3$ composition.

In the present invention, Co or Ni can be used as a diatomic positive ion substitute source for Zn ion. The reason for this is that $CoTiO_3$ and $NiTiO_3$ as well as $ZnTiO_3$ or $MgTiO_3$ also have a hexagonal crystal structure and are able to form a solid solution with respect to Zn ion and Co or Ni ion.

$(Zn_{1-x}M_x)TiO_3$ solid solution has an unstable phase at a high temperature and dissociated into $(Zn_{1-x}M_x)TiO_4$ and TiO_2. When Zn is substituted with Co or Ni, like Mg, hexagonal phase stabilization range is widened, an effect that the present invention intends to attain.

Figures 5A and 5B are graphs showing X-ray diffraction analysis results after $(Zn_{1-x}Co_x)TiO_3$ is calcined at temperatures of 1000°C and 1150°C for four hours, and Figures 6A and 6B are graphs showing X-ray diffraction analysis results after $(Zn_{1-x}Ni_x)TiO_3$ is calcined at temperatures of 1000°C and 1150°C for four hours.

With reference to Figures 2, 4, 5A, 5B, 6A and 6B, in the $(Zn_{1-x}M_x)TiO_3$ (M=Mg, Co or Ni) solid solution, a thermal phase stability is notably $(Zn_{1-x}Mg_x)TiO_3 > (Zn_{1-x}Co_x)TiO_3 > (Zn_{1-x}Ni_x)TiO_3$.

Accordingly, like the $(Zn_{1-x}Mg_x)TiO_3 + xTiO_2$ temperature stable microwave ceramics, the cases of Co and Ni also have the similar effect to the results as shown in Table 1 and 2.

With reference to Figures 5A, 5B, 6A and 6B, it is noted that the lower the thermal treatment temperature is, the lower the stability range of the hexagonal

solid solution is, and a phase stability can be implemented for these compositions in the same manner as shown in Figures 1 and 2.

Figures 7 and 8 respectively show a microwave dielectric characteristic of a test sample that $(Zn_{1-x}Co_x)TiO_3$ and $(Zn_{1-x}Ni_x)TiO_3$, the substitute solid solution of Co and Ni, were sintered at a temperature of 1150°C for four hours.

From the results of Figures 7 and 8, in the $(Zn_{1-x}M_x)TiO_3$ (M = Co or Ni and $0 \leq x \leq 1$) composition, a microwave characteristic having a temperature factor of '0' and excellent dielectric characteristic can be obtained.

In Figures 7 and 8, 'α' region is a co-existence region of $(Zn_{1-x}M)_2TiO_4$ (Cubic) phase and TiO_2 (rutile) phase of Figures 5 and 6, and 'β' region is a co-existence region of $(Zn_{1-x}M_x)_2TiO_4$ (Cubic) phase + (rutile) phase + $(Zn_{1-x}M_x)TiO_3$ (hexagonal) phase, where the condition that the temperature factor is '0' is obtained. The reason for this is that the temperature factors of $(Zn_{1-x}M_x)_2TiO_4$ phase and $(Zn_{1-x}M_x)TiO_3$ phase are respectively negative and the temperature factor of TiO_2 phase is positive, so that a compensation is made for the temperature factors in their suitable mixed phase, and thus, they have the value of '0'.

However, as for the results of Figures 7 and 8, there are problems that the condition that the temperature factor is '0' includes the cubic crystal $(Zn_{1-x}M_x)_2TiO_4$ phase having somewhat low quality factor, that is, having the relatively lower quality factor than the hexagonal crystal $(Zn_{1-x}M_x)TiO_3$, and the composition having the temperature factor of '0' varies according to a sintering temperature.

Accordingly, likewise in the above described embodiment of Table 1 and

2, it is important to perform calcining of powder in $(Zn_{1-x}M_x)TiO_3$ (M = Co or Ni) in the stable range of the hexagonal crystal.

In such a case, the temperature compensation can be possibly performed by properly mixing the hexagonal crystal phase of $(Zn_{1-x}M_x)TiO_3$ having the high quality factor and the negative temperature factor and TiO_2 (rutile) phase having the high quality factor and the positive temperature factor.

Accordingly, likewise of the embodiment of Table 1 and 2, a microwave dielectric having the high quality factor and the stable temperature coefficient can be obtained. That is, a usable microwave characteristic can be obtained from the composition of $(Zn_{1-x}M_x)TiO_3$ and $yTiO_2$ (M is Co or Ni, $0 \leq x \leq 1$, $0 \leq y \leq 0.8$).

The effect of the present invention is not limited thereto. That is, for example, an effect by mixing more than two of A-site atoms constituting the above mentioned ABO_3 type ilmenite phase ceramics can be obtained. Namely, it refers to a mixture of $(Zn_{1-a}Mg_{1-b}Co_{1-c}Ni_{1-d})TiO_3$ ($0 \leq a \leq 1$, $0 \leq b \leq 1$, $0 \leq c \leq 1$, $0 \leq d \leq 1$).

The mixture of $(Zn_{1-a}Mg_{1-b}Co_{1-c}Ni_{1-d})TiO_3$ is calcined (synthesized) in a stable temperature range of the ilmenite phase, into which a suitable amount of TiO_2 (rutile) is added up to $0 \leq y \leq 0.8$, or $(Zn_{1-a}Mg_{1-b}Co_{1-c}Ni_{1-d})TiO_3$ and $yTiO_2$ are mixed by one time and calcined in a stable temperature range of the ilmenite phase.

In this respect, oxide, carbonate, nitrate, alkoxide and the like can be used as a material for ZnO, MgO, CoO and NiO, and anatase or rutile can be used as a material for TiO_2.

INDUSTRIAL APPLICABILITY

As so far described, a high frequency dielectric characteristic having an excellent various temperature compensation varied according to the high quality factor, the dielectric constant and the stable temperature factor and composition but having a very low sintering temperature compared with the conventional dielectric composition can be implemented at a low-priced material such as ZnO, MgO, CoO, NiO or TiO_2.

In addition, since Ag, Cu or their alloy or Ag/Pd alloy can be used as an internal electrode, and thus, can be used as various high frequency devices; i.e., a stacked chip capacitor, a stacked chip filter, a stacked chip capacitor/inductor composite device and a low-temperature sintered substrate, a resonator and a filter or a ceramic antenna.

Especially, the low-temperature sintered composition obtains a remarkably high quality factor more than several times that of the conventional one.

In addition, combination of the almost infinite number of compositions exhibiting the excellent high frequency characteristic can be obtained in the composition range of the present invention.

CLAIMS

1. A high frequency dielectric ceramics composition constituted by combining $(Zn_{1-x}M_x)TiO_3$ and $yTiO_2$ satisfies the conditions of:

wherein M is Mg, Co or Ni,

'x' is $0 \leq x \leq 0.6$ in case of Mg and 'x' is $0 \leq x \leq 1$ in case of Co, and $0 \leq x \leq 1$ in case of Ni, and

$0 \leq y \leq 0.8$.

2. A high frequency dielectric ceramics composition preparation method in which material powder of ZnO, MO (in this respect, MO is MgO, CoO or NiO) and TiO_2 is weighed according to a composition range of $(Zn_{1-x}M_x)TiO_3$ and $yTiO_2$ (M is one of Mg, Co and Ni, x is $0 \leq x \leq 0.6$ in case of Mg, x is $0 \leq x \leq 1$ in case of Co, x is $0 \leq x \leq 1$ in case of Ni, and y is $0 \leq y \leq 0.8$), mixed and dried,

calcined at a temperature of 850~950°C,

the calcined powder is crushed,

the crushed power is shaped,

the shaped body is fired at a temperature of 925~1100°C, and

$(Zn_{1-x}M_x)TiO_3$ is calcined at a temperature corresponding to a region (region II) of below a phase dissociation temperature as shown in Figure 2 to obtain $(Zn_{1-x}M_x)TiO_3$ (M is Mg, Co or Ni) of a single phase of rhombohedral/hexagonal crystal.

3. The method of claim 2, wherein the shaped body is made in a manner that an aqueous solution adding a PVA binder is sprayed onto the crushed powder to make a granule, to which a pressure is applied.

4. The method of claim 3, further comprises a step for maintaining the shaped body at a temperature of 300–500°C for a predetermined time and removing the binder.

5. The method of claim 2, wherein $(Zn_{1-x}M_x)TiO_3$ is first calcined and $yTiO_2$ ($0 \leq y \leq 0.8$) is added to $(Zn_{1-x}M_x)TiO_3$ and then sintered.

6. The method of claim 2, wherein $(Zn_{1-x}M_x)TiO_3$ and $yTiO_2$ are sintered at the same time and sintered.

7. The method of claim 2, wherein TiO2 is anatase or rutile.

8. A high frequency dielectric ceramics composition constituted from combination of $(Zn_{1-a}Mg_{1-b}Co_{1-c}Ni_{1-d})TiO_3$ and $yTiO_2$ ($0 \leq a \leq 1$, $0 \leq b \leq 1$, $0 \leq c \leq 1$, $0 \leq d \leq 1$), and $0 \leq y \leq 0.8$.

9. Various high frequency devices such as a stacked chip capacitor, a stacked chip filter, a stacked chip capacitor/inductor composite device and a module, a low-temperature sintered substrate, a resonator and a filter or a

ceramic antenna, are fabricated by using the dielectric composition of claim 1.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
1 November 2001 (01.11.2001)

PCT

(10) International Publication Number
WO 01/81269 A1

(51) International Patent Classification[7]: C04B 35/46, H01B 3/12

(21) International Application Number: PCT/KR00/00983

(22) International Filing Date: 30 August 2000 (30.08.2000)

(25) Filing Language: Korean

(26) Publication Language: English

(30) Priority Data:
2000-21259 21 April 2000 (21.04.2000) KR

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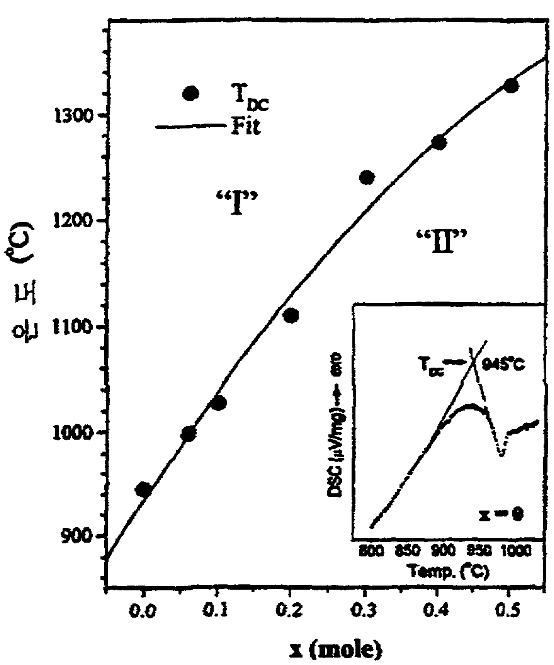
(81) Designated States (*national*): CN, IN, JP, US.

(84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: LOW TEMPERATURE SINTERABLE AND LOW LOSS DIELECTRIC CERAMIC COMPOSITIONS AND METHOD THEREOF



(57) Abstract: A low loss high-frequency dielectric ceramic composition for sintering at a low temperature and method of manufacturing the same which is characterized in that excellent dielectric properties such as a much lower sintering temperature and higher quality coefficient and dielectric constant, compared to a conventional high-frequency ceramic composition, a stabilized temperature coefficient, and a temperature compensating property varied according to a composition, are implemented using a low-priced material such as ZnO-MO (M=Mg, Co, Ni) - TiO_2. In addition, Ag, Cu, an alloy thereof, or an Ag/Pd alloy can be used as an internal electrode. Thus, the composition of the present invention can be used as a dielectric material for all sorts of high-frequency devices, such as a stacked chip capacitor, stacked chip filter, stacked chip capacitor/inductor composite device and module, low temperature sintered substrate, resonator or filter and ceramic antenna.

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FIG 1

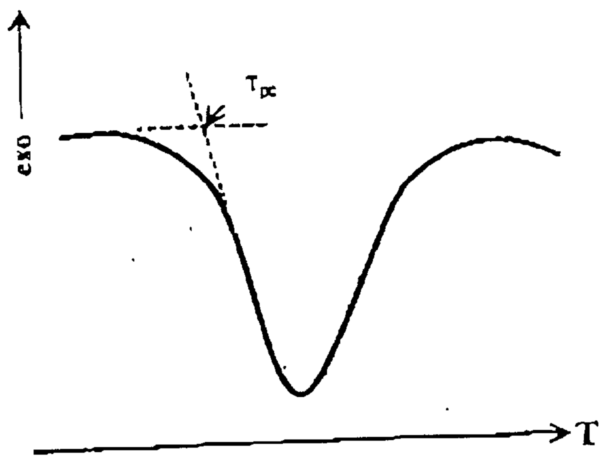

FIG 2

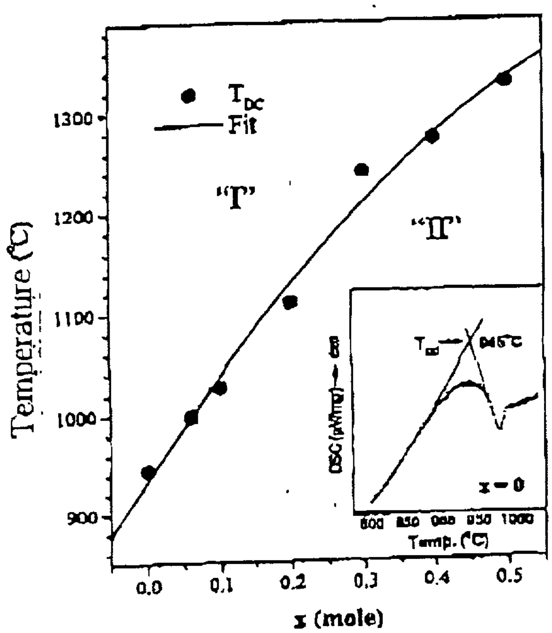

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FIG 3

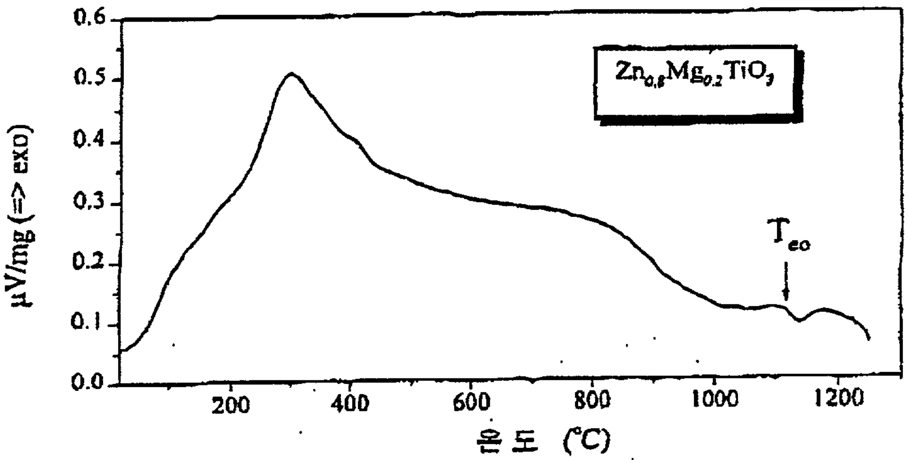

FIG 4

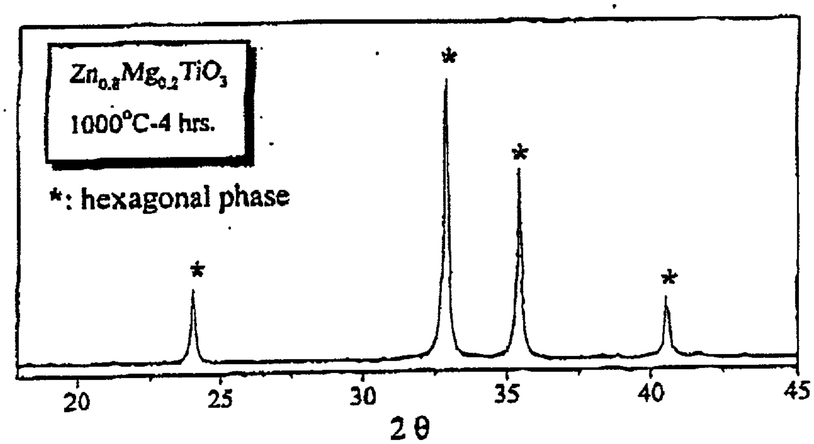

FIG 5A

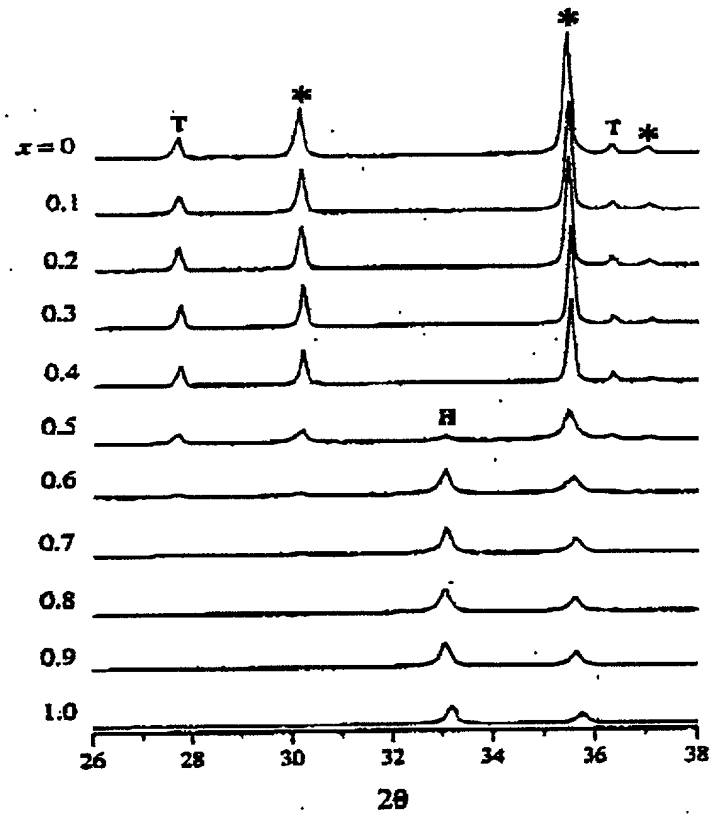

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FIG 5B

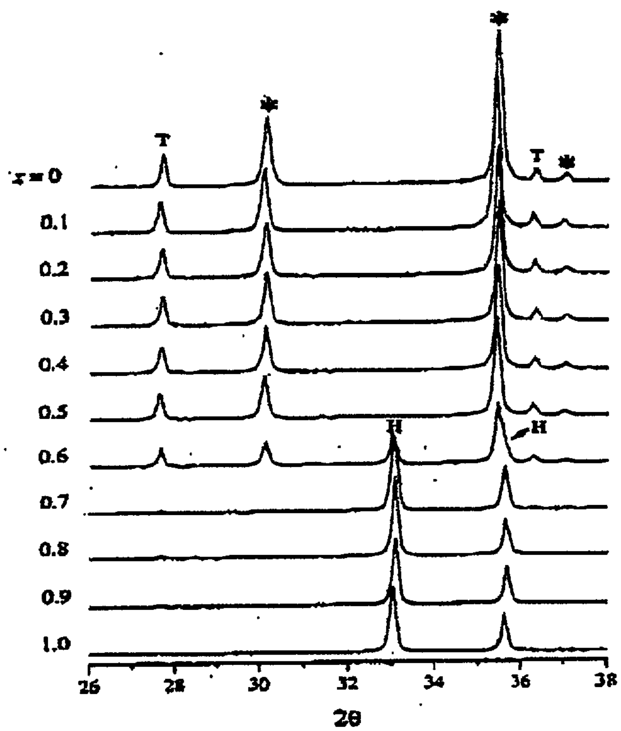

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FIG 6A

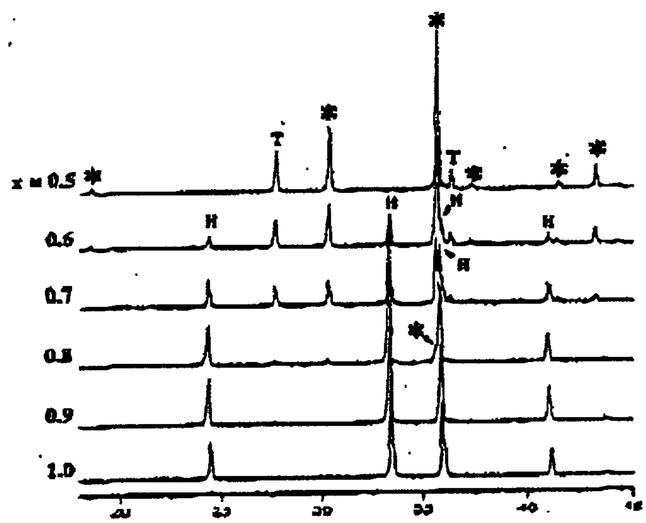

FIG 6B

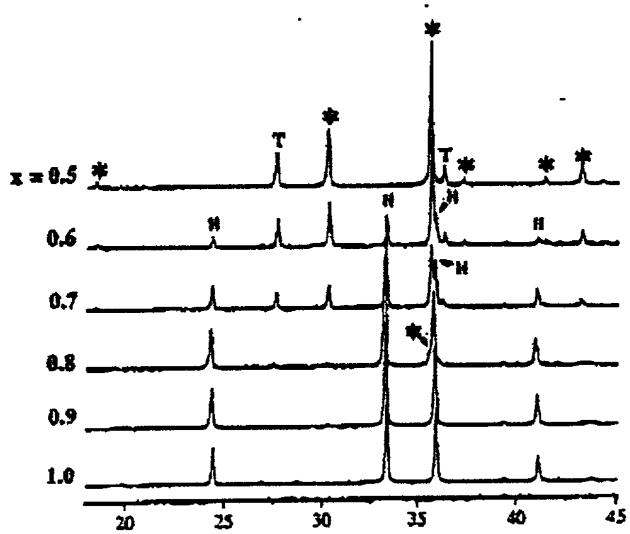

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FIG 7

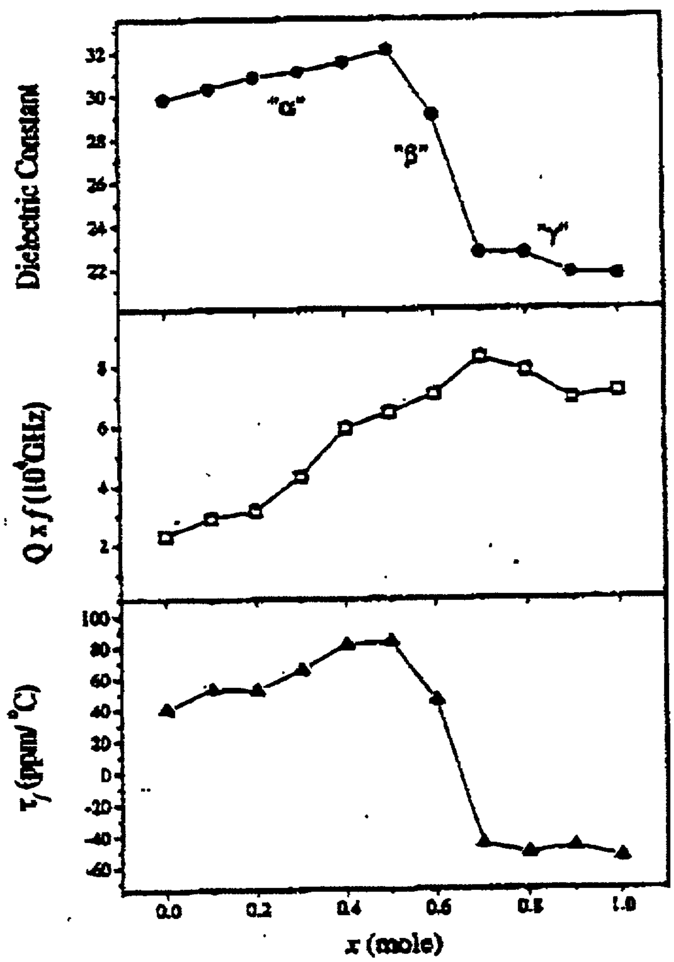
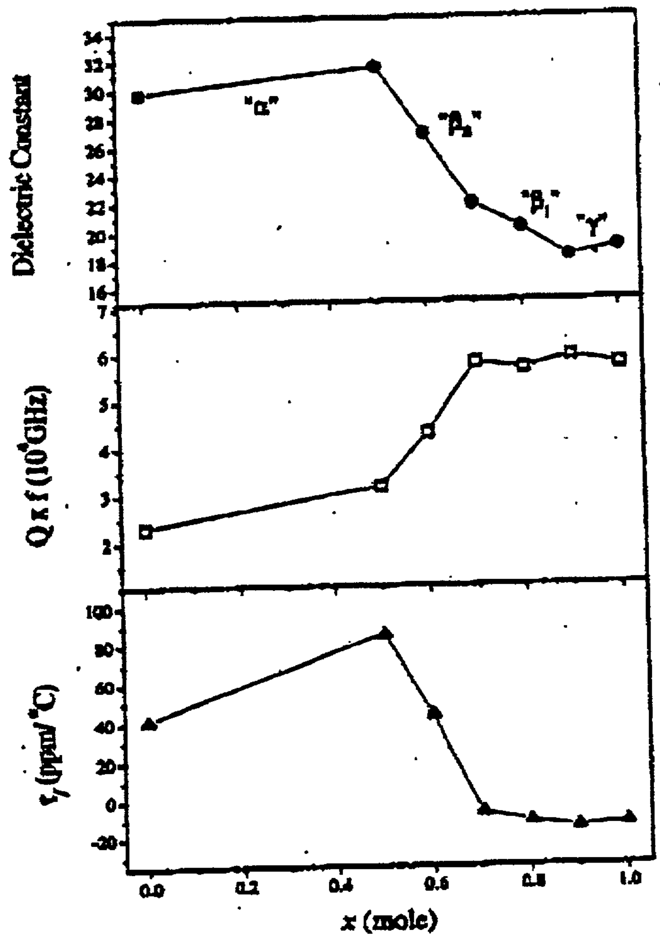


FIG 8


Dielectric Constant
"α"
"β₂"
"β₁"
"γ"
Q x f (10⁴GHz)
τf (ppm/°C)
x (mole)
0.0
0.2
0.4
0.6
0.8
1.0

DECLARATION FOR UTILITY PATENT APPLICATION

AS A BELOW-NAMED INVENTOR, I HEREBY DECLARE THAT:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled: LOW TEMPERATURE SINTERABLE AND LOW LOSS DIELECTRIC CERAMIC COMPOSITIONS AND METHOD THEREOF, the specification of which is attached hereto unless the following box is checked:

☒ was filed on December 20, 2001 as United States Application Serial No. 10/018,426 or PCT International Application No. and was amended on (if applicable).

I HEREBY STATE THAT I HAVE REVIEWED AND UNDERSTAND THE CONTENTS OF THE ABOVE-IDENTIFIED SPECIFICATION, INCLUDING THE CLAIMS, AS AMENDED BY ANY AMENDMENT REFERRED TO ABOVE.

I acknowledge the duty to disclose information which is material to the patentability as defined in 37 C.F.R. § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed:

Application No.	Country	Date of Filing (day/month/year)	Priority Claimed?
2000-21259	Korea	21 April 2000	☒Yes ☐No

I hereby claim benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below:

Application Serial No.	Filing Date

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to

patentability as defined in 37 C.F.R. § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.	Filing Date	Status
PCT/KR00/00983	30 August 2000	☐Patented ☒Pending ☐Abandoned

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

March 22, 2002
Date

1-00

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